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### (54) POLYAMIDE-BASED RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyamide-based resin composition having excellent antistatic characteristics and simultaneously capable of keeping flexibility for a long period, and preventing a plasticizer from bleeding out.

SOLUTION: This polyamide-based resin composition comprises compounding 100 pts.wt. of a polyamide resin with 15-100 pts.wt. of a plasticizer and 5-100 pts.wt. of an electrically conducting filler having a specific surface of  $\geq 500 \text{ m}^2/\text{g}$  (for example, carbon black).

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]Even if this invention is exposed to the thermal excursion of an elevated temperature and low temperature, it can maintain pliability over a long period of time, and it relates to a polyamide system resin composition and a suitable polyamide system resin composition to manufacture the hose for fuel especially excellent in antistatic ability.

[0002]

[Description of the Prior Art]Conventionally the hose for fuel used for motor fuel piping, an automobile oil feeder, an air conditioner, etc., Since there is a possibility of it being charged by friction with fuel, for example, gasoline, gas oil, kerosene, a fuel oil, alcohol, or these mixtures, and generally generating a spark, giving antistatic performances is called for. As a method of giving these antistatic performances, blending conductive bulking agents, such as a carbon system, a metal system, and a metallic-oxide system, is known, and, generally blending carbon black as a carbon system conductivity bulking agent is also performed. The specific surface area of this conductive bulking agent is  $5\text{-}350\text{m}^2/\text{g}$  (specific surface area by a BET adsorption method.) at usual carbon black. When calling it specific surface area in this Description, it is a grade by a BET adsorption method. In preventing electrification of the hose for fuel, it is effective to blend such carbon black, but a hose which has further outstanding antistatic performances is desired.

[0003]Although various kinds of resin is used as a matrix of the resin composition for fuel hose, using polyamide resin from a durable viewpoint over gas oil, gasoline, etc. is proposed. And when using a polyamide resin composition as a charge of hose material, in order to give pliability, addition of a plasticizer is needed, but in order to continue at a long period of time and to maintain pliability, generally it is necessary to blend a lot of plasticizers. On the other hand, when a plasticizer is blended comparatively so much from a viewpoint of only long-term

maintenance of pliability, matrix resin cannot hold a plasticizer but there is a possibility that the bleed out of a plasticizer may arise. Therefore, although the polyamide system resin composition in which the plasticizer effective in the prevention from bleeding was blended with maintenance of pliability is proposed variously, a polyamide system resin composition which continues more at a long period of time, and can maintain pliability, and does not produce the bleeding of a plasticizer more easily is desired.

[0004]Then, this invention has the outstanding antistatic ability, and can maintain pliability over a long period of time, and makes it SUBJECT to provide the polyamide system resin composition in which the bleed out of the plasticizer was controlled.

[0005]

It is means] in order to solve [SUBJECT. In order to solve an aforementioned problem, this invention persons provide the following technical means. That is, this invention relates to the polyamide system resin composition which blends five to conductive bulking agent 100 weight section more than 15 to plasticizer 100 weight section, and specific surface area [ of 500 m ]<sup>2</sup>/g to polyamide resin 100 weight section. The polyamide system resin composition which blends five to conductive bulking agent 100 weight section more than 30 to plasticizer 100 weight section and specific surface area [ of 500 m ]<sup>2</sup>/g to polyamide resin 100 weight section is started. Said plasticizer is applied to the polyamide system resin composition which are at least one sort of compounds chosen from a sulfonamide derivative, a sulfonic ester derivative, a phosphoric ester derivative, a phosphazene derivative, a carboxylic amide derivative, and a carboxylate derivative. Said conductive filler is applied to the polyamide system resin composition which is carbon black. A volume specific resistance value is applied to said polyamide system resin composition which is below 10<sup>8</sup> omega-cm.

[0006]

[Embodiment of the Invention]In the polyamide system resin composition of this invention, various kinds of polyamide resin can be used as polyamide resin used as matrix resin. As the example, the polyamide 6, the polyamide 66, the polyamide 46, the polyamide 11, the polyamide 12, the polyamide 6T, The alloy of two or more sorts of these alloys, such as polyamide MXD6 and amorphous polyamide, and polypropylene resin and polyphenylene sulfide resin can be mentioned. [ these, and ]

[0007]As a plasticizer, at least one sort of compounds chosen from a sulfonamide derivative, a sulfonic ester derivative, a phosphoric ester derivative, a phosphazene derivative, a carboxylic amide derivative, and a carboxylate derivative can be mentioned. These plasticizers have structurally high compatibility with polyamide resin, and the pliability of a polyamide system resin composition can be held also in a cold district.

[0008]Since what can illustrate the alkyl ester of the various carboxylic acid which may be

replaced with a hydroxyl group, a nitro group, an amino group, an epoxy group, halogen, etc., aromatic ester, etc. as a carboxylate derivative, and has a hydroxyl group and an epoxy group has good compatibility with polyamide, it is preferred. As an example of a carboxylate derivative, For example, dimethyl phthalate, diethyl phthalate, di-n-octyl phthalate, Diphenyl phthalate, benzyl phthalate, dimethoxyethyl phthalate, 4,5-epoxy hexahydrophthalic acid di(2-ethylhexyl), 4,5-epoxy cyclohexa \*\*\*\*\* (7,8-epoxy-2-octenyl), 4,5-epoxy cyclohexa \*\*\*\*\* (9,10-epoxy octadecyl), 4,5-epoxy cyclohexa \*\*\*\*\* (10,11-epoxy undecyl), Phthalate ester derivatives, such as an ethylene oxide addition of \*\*\*\*\* (tetrahydro full FURIROKISHI ethyl), various phthalic acid mixed ester, and phthalic acid mixed ester, An isophthal acid ester derivative, a tetrahydrophthal acid ester derivative, Para hydroxybenzoic acid butoxyethyl, Para hydroxybenzoic acid cyclohexyloxyethoxyethoxyethyl, Benzoic ester derivatives, such as a Para hydroxybenzoic acid addition of Para hydroxybenzoic acid 2-ethylhexyl, hydroxybenzoic ester of omega-alkyl oligo ethylene oxide, and undecyl glycidyl ether, Propionate ester derivatives, such as \*\*\*\*\* (tetrahydro full FURIROKISHI ethyl), An adipate derivative, an azelate derivative, a sebacic acid ester derivative, A dodecane-2-acid ester derivative, an ester maleate derivative, a fumarate ester derivative, A TORIMETTO acid ester derivative, tri citrate (butoxyethoxyethyl), Mono- [ citrate di-n-octyl ] (nonylphenoxyethyl), tri citrate n-octyl, Citrate dioctyl (tetrahydro full FURIROKISHI ethyl), tri citrate Millis Chill, Citrate derivatives, such as triethyl citrate, an itaconic acid ester derivative, Oleic acid ester derivatives, such as tetrahydrofurfuryl oleate, A recinoleic acid ester derivative, lactic acid (n-butyl), lactic acid (2-ethylhexyl), Lactic acid (n-butoxyethoxyethyl), lactic acid (n-octoxy ethoxyethyl), Tartrate derivatives, such as lactate derivatives, such as lactic acid (n-decyloxy ethoxyethyl), tartaric acid II (octoxy ethoxyethyl), tartaric acid (n-octyl) (nonylphenoxyethyl), and tartaric acid II (octoxy ethoxyethyl), Salicylic acid ester derivatives, such as apple acid ester derivatives, such as dibutoxyethyl malate, di(n-butoxyethyl) malate, distearyl malate, and malic acid octadecenyl isononyl, and a salicylic acid addition of benzyl glycidyl ether, etc. can be illustrated.

[0009]As a phosphoric ester derivative, trimethyl phosphate, triethyl phosphate, Tributyl phosphate, tri-(2-ethylhexyl) phosphate, 2-ethylhexyl diphenyl phosphate, tributoxyethyl phosphate, Triphenyl phosphate, cresyl diphenyl phosphate, isodecyldiphenylphosphate, Tricresyl phosphate, trixylenyl phosphate, Tori (chloroethyl) phosphate, xylenyl diphenyl phosphate, the tetrakis (2,4-ditertiary-butylphenyl) 4, 4'-biphenylene diphosphonate, etc. can be illustrated. As an example of a phosphazene derivative, Hexaphenoxy cyclotriphosphazene, octaphenoxy cyclotetraphosphazene, Decaphenoxy cyclopentaphosphazene, hexapropoxy cyclotriphosphazene, Annular phosphazene compounds, such as octa pro POKISHIKISHI cyclotetraphosphazene and decapropoxy cyclopentaphosphazene, The chain phosphazene compound which replaced the propoxy group and/or the phenoxy group by chain

dichlorophosphazene, 4,4'-sulfonyldiphenylene (bisphenol S residue), a 4,4'-oxydiphenylene group, a 4,4'-thiodiphenylene group, a 4,4'-diphenylene group, etc. can be mentioned. An amino group and/or a phenylamino group may replace these phosphazene derivatives by arbitrary positions. Said one kind may be independently used for these phosphazene derivatives, and two or more sorts of mixtures may be used for them. It may be a mixture of annular phosphazene and straight-chain-shape phosphazene.

[0010]N-cyclohexylbenzoic acid amide etc. can be illustrated as a carboxylic amide derivative. As a sulfonamide derivative, N-methyl-benzenesulfoamide, N-ethyl benzene sulfoamide, N-butyl-benzenesulfoamide, N-cyclohexyl-benzenesulfoamide, N-ethyl-p-toluene sulfoamide, N-butyl-toluene sulfoamide, N-cyclohexyl-toluene sulfoamide, etc. can be illustrated. Ethyl benzenesulfonate can be illustrated as a sulfonic ester derivative.

[0011]It is good to consider it as 15 or more weight sections to matrix resin 100 weight section from a viewpoint of securing sufficient pliability over a long period of time as loadings to matrix resin of these plasticizers, and it is still more preferred to consider it as 30 to 100 weight section.

[0012]5-100 weight-section combination of the conductive bulking agent more than specific surface area [ of 500 m ] <sup>2</sup>/g is carried out at the resin composition of this invention. The maximum of specific surface area is usually a 1300 m<sup>2</sup>/g grade. Especially as an example of this conductive bulking agent, the thing of specific surface area [ of 900-1300 m ] <sup>2</sup>/g can be illustrated among Ketchen black, channel black, etc. Here, the specific surface area of usual carbon black is a 5-350 m<sup>2</sup>/g grade. For example, the specific surface area of acetylene black is a 15-100 m<sup>2</sup>/g grade, the specific surface area of furnace black is a 15-300 m<sup>2</sup>/g grade, and the specific surface area of thermal black is a 5-30 m<sup>2</sup>/g grade. Generally the specific surface area of conductive bulking agents other than carbon black is smaller than carbon black, and is a less than at most 100 m<sup>2</sup>/g grade. Thus, the conductive bulking agent used by this invention has the feature in the point of having very big specific surface area.

[0013]The conductive bulking agent used in this invention has the operation which holds a plasticizer component stably in polyamide resin, and does so the effect that the bleed out of the effect of maintaining pliability over a long period of time by this operation, and a plasticizer can be controlled notably. It is for that the loadings of the conductive bulking agent more than specific surface area [ of 500 m ] <sup>2</sup>/g are specified as five to 100 weight section also making this operation effect fully reveal, and if there are too few loadings, since pliability cannot fully be held and fear of the bleed out of a plasticizer is produced, it is not desirable. If loadings exceed 100 weight sections, since there is a possibility of spoiling the physical properties of a resin composition and spoiling pliability on the contrary, it is not desirable. In this invention, as

long as specified quantity combination of said conductive bulking agent is carried out, it aims at adjustment of conductivity, or improvement of physical properties, Using together the conductive bulking agent which separates from the aforementioned regulation does not interfere, either, and as this conductive bulking agent, Carbon, such as carbon black and a carbon fiber, a potassium titanate fiber, Powder or textiles, such as what covered the surfaces, such as titania textiles, a silica fiber, wollastonite, and mica, with conductive substances, such as carbon, tin oxide/antimony oxide, iron, nickel, copper, silver, gold, and aluminum, etc. can be illustrated.

[0014]As for the loadings of these conductivity bulking agent, it is preferred to set up from a viewpoint of antistatic performances, so that a volume specific resistance value may become as a resin composition below in  $10^8$  omega-cm, and it is preferred that below  $10^6$  omega-cm especially carries out. The minimum of a volume specific resistance value is a  $10^2$  omega-cm grade. In addition to said each ingredient, other ingredients can be blended with the resin composition of this invention in the range which does not spoil the effect of this invention. The hindered amine system for the weatherproof improvement as an example of this ingredient, Ultraviolet ray absorbents, such as a benzotriazol system, iodination copper of an inorganic system, a cuprous chloride, The fibrous filler for the color for the Silang system coupling agent for raising the release agent for fire retardant, such as aluminium hydroxide for the elastomer for a shock-proof improvement and fire-resistant improvement, and the improvement in a moldability and the compatibility of each ingredient and coloring, paints, and the improvement in a mechanical strength, etc. can be illustrated.

[0015]Although there is no restriction in particular when manufacturing the resin composition of this invention and it can manufacture in accordance with a publicly known manufacturing method conventionally, For example, it can carry out by the method of supplying each ingredient from the hopper with which the kneading machine was the same or different, a plunger, etc., etc., kneading the method and resin which carry out melt kneading with a twin screw extruder etc., after mixing each ingredient using a mixer, a blender, etc. beforehand. Although the resin composition of obtained this invention may be directly fabricated in the shape of a hose, in the state where it pelletized by the pelletizer, it may be kept and may once be circulated.

[0016]When manufacturing the hose for fuel using the resin composition of this invention, according to the kind etc. of fuel to deal with, it can fabricate on a monolayer or the multilayer hose for fuel. When considering it as the hose of a monolayer, it can fabricate by injection molding, extrusion molding, blow molding, etc. In considering it as the multilayer hose for fuel, (1) innermost layer Fluoro-resins, such as polyvinylidene fluoride and polytetrafluoroethylene, It is considered as the resin which has sour gasoline-proof nature, such as epichlorohydrin rubber, The outermost layer is made into protective layers, such as nitrile rubber, acrylic

rubber, polyethylene, and polyvinyl chloride, The hose for fuel of the three-tiered structure which prepares an interlayer the resin composition of this invention, and (2) inner layers are used as the resin which has sour gasoline-proof nature, such as a fluoro-resin, and the hose for fuel of the two-layer structure of providing the resin composition of this invention for an outer layer, etc. can be illustrated. It is good also as multilayer structure more than a three-tiered structure on the basis of these. A textiles braid reinforcement layer may be provided between each class.

[0017]The resin composition of this invention has the outstanding heat resistance and antistatic ability.

Since pliability is maintained over a long period of time, it can use conveniently especially as a resin composition of the hose for fuel used for motor fuel piping, an automobile oil feeder, an air conditioner, etc.

The resin composition of this invention can be conveniently used also as parts of the circumference of the engine of cars, such as an air intake, V bank covering, and a cylinder head cover.

[0018]

[Example]Working example and a comparative example are given to below, and this invention is explained still in detail.

[0019]The following were used in this example.

PA11: Polyamide 11 resin (a trade name "Nylon 11", the Toray Industries, Inc. make).

Plasticizer A: Carboxylate system plasticizer (butoxyethyl para-hydroxybenzoate).

Plasticizer B: Carboxylate system plasticizer (2-ethylhexyl para-hydroxybenzoate).

Plasticizer C: Carboxylic amide system plasticizer (N-cyclohexyl-benzoic acid amide).

Plasticizer D: Sulfonamide series plasticizer (N-cyclohexyl-benzenesulfonamide).

Plasticizer E: Phosphazene system plasticizer (hexaphenoxy cyclotriphosphazene).

The conductive bulking agent A: The specific surface area measured with the BET adsorption method is carbon black (a trade name "Ketchen black EC DJ-600", the product made by AKUZOKEMI) of  $1250 \text{ m}^2/\text{g}$ .

The conductive bulking agent B: The specific surface area measured with the BET adsorption method is carbon black (trade name "Ketchen black EC normal grade", product made by AKUZOKEMI) of  $950 \text{ m}^2/\text{g}$ .

The conductive bulking agent C: The specific surface area measured with the BET adsorption method is carbon black (made by trade name "Vulcan XC-72" Asahi carbon incorporated company) of  $250 \text{ m}^2/\text{g}$ .

The conductive bulking agent D: What (a trade name "DENTORU WK-500", the Otsuka Chemical Co., Ltd. make) provided tin oxide / antimony oxide system conductive coat in the

surface of monoclinic system titania textiles (the mean fiber diameter of 0.4 micrometer, 12 micrometers of mean fiber length).

[0020]Working example 1-8 and a 2-445 mm of comparative example phi twin screw extruder were used, it was set as the resin temperature of 190 \*\*, the polyamide resin fully beforehand dried from the main hopper was thrown in, and the conductive bulking agent was thrown in from the twin screw extruder side hopper. With the plunger pump, it pressed fit, and the plasticizer was pelletized continuously, and the resin composition of working example 1-8 and the comparative examples 2-4 was obtained. The presentation (the weight section shows) of the resin composition of working example 1-8 and the comparative examples 2-4 is as in Table 1. The comparative example 1 consists only of polyamide resin. The obtained pellet is used and it is JIS K 7113 by an injection molding machine. The No. 1 type specimen was manufactured, respectively. The tube of the diameter 8.4 phi of a result was fabricated for the obtained pellet on 2.7-m the conditions for /in taking over speed using the 30 mmphi extrusion machine (ratio-of-length-to-diameter=22), respectively by resin temperature [ of 190 \*\* ], mandrel 7.4 phi, die/chips 10phi/10phi, and extrusion rate/of 37.8g.

[0021]According to JIS K 6911, the volume specific resistance value (ohm-cm) was measured about the resin composition of measurement working example 1-8 of a volume specific resistance value, and the comparative examples 1-4.

According to JIS K 7113, tensile fracture elongation (%) was measured about tensile fracture extension test each specimen.

After covering tensile fracture extension test each specimen after aging over aging for 120 \*\* and 14 days, tensile fracture elongation (%) was measured according to JIS K 7113.

The appearance of the tube of existence each working example of bleeding and a comparative example was observed, and the existence of bleeding was judged by viewing. These results are combined with Table 1 and shown.

[0022]

[Table 1]



	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	比較例1	比較例2	比較例3	比較例4
樹脂	100	100	100	100	100	100	100	100	100	100	100	100
可塑剤A	30	30	30	50						10	30	30
可塑剤B					30							
可塑剤C						30						
可塑剤D							30					
可塑剤E								30				
導電性充填剤A	20											
導電性充填剤B		20	10	20	20	20	20	20		20		
導電性充填剤C											20	
導電性充填剤D			10									20
体積固有抵抗値( $\Omega \cdot \text{cm}$ )	$10^2$	$10^4$	$10^7$	$10^5$	$10^4$	$10^4$	$10^4$	$10^4$	$>10^{10}$	$10^3$	$10^8$	混雑困難
引張伸び(試験前)	200	250	260	300	250	240	240	230	20	90	200	混雑困難
引張伸び(経時試験後)	140	160	180	250	160	160	150	140	20	60	140	混雑困難
ブリード有無	無し	無し	無し	無し	無し	無し	無し	無し	無し	無し	有り	—

[0023]

[Effect of the Invention]As mentioned above, the polyamide system resin composition concerning this invention has the more outstanding antistatic ability, and can maintain pliability over a long period of time, and the bleeding of a plasticizer does not produce it easily. This resin composition is preferred as a raw material of the hose for fuel used for motor fuel piping etc.

[Translation done.]